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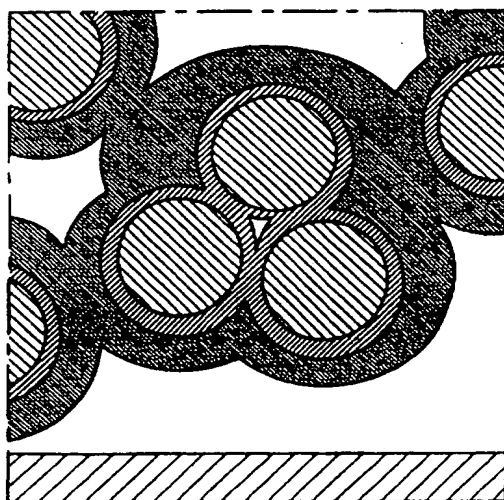
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(54) Title: PRINTABLE COMPOSITIONS, AND THEIR APPLICATION TO DIELECTRIC SURFACES USED IN THE MANUFACTURE OF PRINTED CIRCUIT BOARDS



- ☐ EPOXY RESIN
- ☒ Cu
- ☒ Sn 63 / Pb37
- ☒ Cu₃ Sn / Cu₆ Sn₅
- ☒ FR-4 SUBSTRATE

(57) Abstract

A composition for use in the production of metal traces and other metal components of printed circuit boards, wiring boards and the like comprises the following components: (a) a metal powder, (b) a solder powder, (c) a polymer or a monomer which is polymerisable to yield a polymer, a said polymer being cross-linkable under the action of a chemical cross-linking agent, and (d) a chemical cross-linking agent for said polymer, the cross-linking agent having fluxing properties and being unreactive with the polymer without catalysis. The polymer will generally be an epoxy resin and the cross-linking agent will generally be a polyacid. The composition preferably is one in which the metal powder and/or solder powder generates and/or has adhered thereto a catalyst for the cross-linking agent which is liberated on application of heat.

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PRINTABLE COMPOSITIONS, AND THEIR APPLICATION TO
DIELECTRIC SURFACES USED IN THE MANUFACTURE
OF PRINTED CIRCUIT BOARDS

5 The present invention relates generally to printed circuit board (PCB) production and to inks and other compositions to be applied to dielectric substrates in PCB production. The present invention particularly relates to ink and other compositions that are
10 conductive by virtue of containing metal(s), and to the use of such conductive compositions in the manufacture of printed circuit boards.

 It is well established that printed circuit boards offer highly cost effective and space saving
15 improvements when used in electrical devices. Prior to the advent of printed circuit boards, it was necessary to run individual wires between each component used in an electrical device. The advent of printed circuit board technology permitted manufacturers who repeatedly
20 utilized the same complex circuit design in a high volume product to (i) eliminate the individual wiring of each component into the system while (ii) providing an integral mechanical support for the circuitry.

 More particularly, a printed circuit board may
25 have numerous electrically conductive pathways imprinted on a dielectric substrate, most frequently a glass fibre reinforced phenolic or epoxy resin substrate. The electrical components may then be attached to the printed circuit board with the
30 conductive patterns on the board forming electrical connections thereon.

 Heretofore, conventional methods of forming electrical pathways on a printed circuit board were both expensive and time consuming. For example, in one
35 process, the dielectric substrate is coated over its entire surface with a sheet of conducting metal, such

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as copper or aluminum. This is generally accomplished by utilizing an electroplating technique. The selected pattern or matrix, which will represent the electrical pathways between the components, is then cut into a cloth material such as silk. The cloth material, having the cut-out matrix is then placed on the dielectric substrate which has been previously coated with the conducting material. An etch-resist ink is then rolled over the cloth, with the ink passing through the cut-out pattern and forming an inked matrix on the coated dielectric substrate. The above described method is a conventional silk screen technique. The inked and coated board is then exposed to light which causes the etch-resist ink to become acid resistant. The dielectric substrate is then treated with acid such that all of the metal areas of the board not coated with the ink are etched away leaving just the matrix pattern. The ink itself may then be removed by conventional techniques, thereby leaving the electrically conductive pathways formed on the printed circuit board.

In another method used in the prior art, a catalyst is placed on an uncoated dielectric substrate in the desired wiring pattern. The substrate is then immersed in a charged solution of copper ions, such that the electrical pathways are formed by electrodeposition in the areas where the catalyst was placed.

The conventional methods are (i) time consuming, (ii) expensive, (iii) wasteful of materials and (iv) produce environmentally hazardous and toxic chemicals, primarily spent acids. Not only are numerous steps performed by skilled personnel necessary to produce a printed circuit board, but great amounts of conducting metal are needed for coating an entire dielectric substrate, or to provide an ionic solution.

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With a view to seeking simpler and safer application methods for the production of conductive pathways on PCB's, a number of documents have been noted.

5 Thus, U.S. Patent No. 4,696,764 discloses use on a dielectric substrate of an electrically conductive adhesive composition having two types of electrically conductive particles with an average particle diameter of at least 1 micron (1 μ m). The second type of
10 particles need not be of the same material as the first, and have an average particle diameter of not more than 0.5 μ m. U.K. Patent Application GB 2054277 discloses use on a dielectric substrate of a pressure-sensitive electroconductive elastic body of a matrix of
15 electrically insulating material with a metal powder having particular densities, packing fraction, susceptibility to flow and bulk.

 From U.S. Patent No. 4,740,252, there is known a solder paste making use of conductive metallic
20 particles which may be silver, nickel or copper. If copper is used, the particles should be coated with nickel so as to make the surface wettable and to prevent formation of a brittle intermetallic compound on the surface of the particles. In the same field,
25 U.S. Patent No. 4,888,135 discloses an electrically conductive composition containing copper particles with a silver coating and a titanate coupling agent combined to the copper particles and/or the silver coating material. Moreover, U.S. Patent No. 4,732,702
30 discloses an electroconductive resin paste comprising an epoxy resin formed by condensation of a bisphenol compound and a butadiene compound having carboxylic acid terminal groups and an electroconductive filler. The bisphenol compound may be a halogenated bisphenol A
35 reacted with epichlorohydrin.

 Japanese Patent 0133799 discloses a conductive

paint containing a mixture of binder (such as epoxy resin), conductive metal powder and solder. The abstract of the patent discloses that, when copper is the conductive metal, a binder having fluxing function, such as epoxy-acrylic or phenol resin, is used to remove oxide film on the copper particles. The inventive technique in this document operates by connecting the conductive metal powder to fused solder powder by way of heat treatment, the conductive metal powder and solder powder having a flake shape, and uniformly mixing the composite of conductive metal powder thus produced and solder powder with the binder so as to form a low resistance conductor.

Japanese Patent 0160072 discloses an electroconductive adhesive composition containing copper powder, solder powder and a binder resin. Dependent claims further define this conductive adhesive material as being characterized by a weight ratio of the copper powder to the solder powder preferably in the range from 10:5 to 10:1, and with the solder powder being in semi-molten state at the curing temperature of the thermosetting resin.

Japanese Patent Application JP 57-113505 concerns, more specifically, a conductive ink which may comprise solder-plated copper powder, solder powder, an activating agent, and an organic resin. This conductive composition has a weight ratio of the solder-plated copper powder to the solder powder in the range between 40:60 to 90:10.

U.S. Patent No. 4,564,563 discloses a solderable composition having silver flakes in a matrix formed from acrylic, vinyl and epoxy monomers.

U.S. Patent No. 4,678,602 discloses a highly conductive styrene resin composition containing a copolymerized unsaturated dicarboxylic acid anhydride and a metallic filler.

U.S. Patent No. 4,775,500 discloses a method of making an electrically conductive polymeric composite with carbon black as electrically conductive filler.

5 U.S. Patent No. 4,786,437 discloses particle filled compositions making use of a pacifier, such as an organotin compound or sulphur bearing compounds, as an interfacial agent between conductive particles and a polymer matrix.

10 U.S. Patent No. 4,830,779 discloses an electrically conductive resin composition comprising a resin, a metallic powder, a diphosphonic acid derivative and an alcohol.

15 U.S. Patent No. 4,874,548 discloses an electrically conductive adhesive composition comprising an epoxy resin and conductive fibers.

Finally, United States Patent No. 5,376,403 concerns electrically conductive adhesive compositions, and methods for the preparation and use thereof, in which a solder powder, a chemically protected cross-linking agent with fluxing properties and a reactive monomer or polymer are the principal components. Depending upon the intended end use, the compositions comprise various combinations of a relatively high melting powder; solder powder; the active cross-linking agent which also serves as a fluxing agent; a resin; and a reactive monomer or polymer. The compositions are useful as improved conductive adhesives, such as for attaching electrical components to electrical circuits: the compositions comprising metal powder with high melting metals are ideally suited for creating the conductive paths on printed circuits. The compositions for forming conductive paths may first be applied to a substrate in the desired pattern of an electrical circuit, and then heated to cure it. During heating, 35 the action of the cross-linking agent and optional reactive monomer or polymer within the mixture fluxes

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the metals, enabling sintering to occur between the metal powder and the solder powder.

Attempts to produce conductive inks as a source of conductive traces to replace conventionally produced conductive traces of printed circuit boards have not met with commercial success for several reasons:

The electrical conductivity of metal filled polymer inks (Polymer Thick Film inks) as exemplified in US Patents 4,740,252; 4,888,135; 4,732,702; 4,678,602; 4,564,563; 4,725,500; 4,786,437 and electrically conductive adhesive compositions 4,830,779 and 4,874,548 is inherently very low, typically about 1% or less of copper film. This creates excessive resistance, and heat, in most circuits, limiting the use of this technology to low performance "niche" applications. Additionally, these products are not solderable, limiting their use only to applications that do not require subsequent assembly operations.

The electrically conductive compositions taught in Japanese Patents 0133799 and 0160072, and Japanese Patent Application JP 57-113505 provide improved electrical conductivity and solderability when compared to polymer thick films, but suffer from severe disadvantages as well.

Thus, while the electrical conductivity is improved, but only marginally, the chemical cross-linking (curing) of the resin begins well in advance of solder melting temperatures, increasing viscosity of the flux (which hinders the flux's ability to carry away oxides) and decreasing the concentration of active fluxing sites, which have been neutralised by reaction with resin. This results in electrical conductivity being improved only by a factor of 2 or less in relation to polymer thick film compositions.

These compositions are also based on relatively large metal particles which preclude their use in

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printing fine line circuits. As virtually all circuit boards produced today have traces of 250 microns or less, these products will have a very limited utility. Since the surface area of metal particles increases exponentially as particle size is reduced, the inks made from fine ($\leq 10\mu$) particles have substantially more surface area, and consequently, substantially more metal oxides that need to be removed to facilitate metallic union, or sintering of the composition. As metallic powders become finer (smaller particles) more aggressive fluxing agents are needed to remove these oxides. The known compositions, therefore, require the addition of very strong fluxing materials and activators to allow the use of fine particles, and fine line printed circuits. These aggressive fluxing materials, and their decomposition products remain in the circuit trace, and can extensively damage the circuit by corrosion, of the metals and degradation of the polymer, and be a source of ionic contamination which will prematurely fail the circuit and electronic assembly.

These strong fluxing agents are also very reactive with the adhesive resins used in these inks, creating a stability problem for the ink composition. These products must thus be used very soon after they are mixed.

The electrically conductive composition described in US Patent 5,376,403 provided a marked improvement over earlier technology by improving electrical conductivity to 10% of that of copper, an order of magnitude improvement over PTF, and by providing a solderable composition that could be printed to produce fine line circuitry, but this product is not without major disadvantages. Thus, printed circuits produced with this material must be processed in an inert environment, preferably a vapour phase soldering

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machine wherein the heating takes place in the vapour
of a high temperature fluorinated fluid. This
equipment is expensive, expensive to operate, and
scarcely used in the printed circuit industry, limiting
the utility of the composition. Moreover, the ink
described is based on extensive use of brominated
aromatic materials, which at the present time are
subject to extensive inquiry into their effects on
human health. A proposal has been made to ban their
use in the European Polymers Industry.

Additionally, the use of alcohols to esterify the
fluxing agent (and chemically protect it) is
reversible, and the alcohol is regenerated as a
substantial part ($\approx 50\%$) of the adhesive, weakening the
bond strength and making the circuit liable to chemical
attack.

The processing conditions described for the
composition of USP 5,376,403 require an involved
thermal profile which includes curing at 215°C and
postcure at 150°C . These conditions promote the
formation of intermetallic compositions known to degrade
the performance of electrical conductors and
interconnects by both increasing the resistance to
current flow, and embrittling the trace. This problem
is exacerbated by additional thermal processing, as is
required to produce electronic assemblies.

Accordingly, it is an object of the present
invention to provide improvements in the PCB production
technology and, in particular, conductive ink
compositions and precursors thereof which enable
printed circuits to be produced quickly on a low-cost
basis appropriate for both short and long production
runs.

It is also an object of the present invention to
provide improvements in the production of printed
circuits with the aim generally of producing fully

additive multilayer interconnection.

In one aspect, this invention provides a composition of matter comprising the following components:

- 5 (a) a metal powder,
- (b) a solder powder,
- (c) a polymer or a monomer which is polymerisable to yield a polymer, a said polymer being crosslinkable under the action of a chemical
- 10 cross-linking agent,
- (d) a chemical cross-linking agent for said polymer, the cross-linking agent having fluxing properties and being unreactive with the polymer without catalysis,
- 15 which metal powder and/or solder powder generates and/or has adhered thereto a catalyst
- (e) for the cross-linking agent which is liberated on application of heat.

Component (a) is typically a metal powder of high

20 melting point and high electrical conductivity.

Component (b), by being a solder powder, is a low melting point constituent. Component (c) is preferably an epoxy resin, in particular a B stage epoxy resin. Component (d) is typically a polyacid to be described

25 in detail hereinafter. Finally, component (e) may be an azole, such as benzotriazole, applied to powder (a) in particular as a stability enhancer.

This invention provides, in a second aspect, a composition on, or for application to, a dielectric

30 substrate in a predetermined pattern comprising, in admixture

- (i) a metallic powder component which includes (a) a high melting point constituent of high electrical conductivity and (b) a relatively low
- 35 melting point constituent; and
- (ii) a polyacid effective as a fluxing agent for the metallic powder component and as a cross-

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linking agent for an epoxy resin at a first temperature and at a higher second temperature, respectively, the polyacid being in contact with such epoxy resin.

5 Compositions embodying this invention will be described hereinafter in detail and in their uses in terms of those according to the second aspect of the invention. However, it should be noted that compositions according to the first aspect of the
10 invention have, through their embodying the same inventive principle, like uses.

 The epoxy resin is generally an additional component of the composition when it is to be a conductive ink composition for use in the production of
15 a printed circuit board. Alternatively, in producing a printed circuit board, an epoxy resin may be applied to a dielectric substrate by, for example, curtain coating or by patterning as a glue line and caused to interact with the metallic powder/polyacid combination of the
20 composition subsequently applied to the dielectric surface.

 The composition described herein can be processed in readily available air environment furnaces, contains no environmental or health damaging materials, and
25 requires no post curing (intermetallic producing) processing.

 In a third aspect, this invention provides a method of making an electrically conductive circuit on a dielectric surface comprising patterning a substrate
30 with the admixture of metallic powder component and polyacid as aforesaid according to the second aspect of the invention, with either the epoxy resin being pre-coated on the substrate or the epoxy resin being incorporated in the patterned composition, and heating
35 the admixture thus patterned to a temperature above the melting point of the low melting point constituent but below the melting point of the high melting point

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constituent, being a temperature at which the polyacid is catalyzed by oxides liberated from the metallic powder, to achieve substantially complete crosslinking of the epoxy resin. When, as will be described
5 hereinafter, the metallic powder is treated with an azole such as benzotriazole, such temperature will also be one at which the azole is liberated to take part in catalysis of cross-linking of the epoxy resin.

In a fourth aspect, this invention provides an
10 electrically conductive circuit which comprises a metal film patterned upon a dielectric substrate and adhesively adhered thereto by a cured and cross linked epoxy resin, the metal film resulting from the patterning on the substrate of a composition comprising
15 in admixture, (i) a metallic powder component which includes (a) a high melting point constituent of high electrical conductivity and (b) a relatively low melting point constituent and (ii) a polyacid effective as a fluxing agent for the metallic powder component
20 and a cross-linking agent for an epoxy resin, an epoxy resin having been coated or patterned onto the dielectric substrate prior to patterning of said film. Upon heating to a temperature sufficient to melt the
25 solder powder, the polyacid will flux the metallic powders, absorbing the liberated catalysts, and contact and mix with the pre-catalysed epoxy resin at the substrate / metallisation interface, incorporating and cross-linking said epoxy resin to provide a strongly
30 adhered patterned metallisation upon the substrate surface. Preferably the epoxy resin is either one which is as a B stage resin or is a resin which can be B staged after application.

When practising the invention in accordance with its second, third and fourth aspects, reliance is
35 placed on the co-use of the three components, components (i) and (ii) identified above and an epoxy resin. In this context, hereinafter, the term "ink"

will be used to denote printable compositions comprising components (i) and (ii) as aforesaid and which usually, but not always, will contain epoxy resin. A sophisticated relationship has been found to exist between these components in that the polyacid (ii) serves as a fluxing agent for the metallic powder component (i) so as to produce a metal oxide in sufficient amount so that, at elevated temperatures, it serves to catalyse a reaction between the epoxy resin and the polyacid (ii) then acting as curing agent. Although a simple acid could serve as a fluxing agent, a polyacid is necessary in the conductive ink composition in order to achieve cross-linking at two or more bonds of the epoxy resin.

Starting with the simplest component, the epoxy resin is preferably one which is liquid at ambient temperature and serves as an adhesive. The preferred epoxy resin is either a diglycidyl ether of bisphenol A or a diglycidyl ether of bisphenol F.

The polyacid is preferably a polycarboxyl compound which serves as a fluxing agent for the metallic powders which produce metal oxide which is in turn a catalyst for reaction between the epoxy resin and the carboxyl groups of the polymer at elevated temperatures. Such polycarboxyl compound may be a carboxylated polymer, a polycarboxylic acid or a polymer fatty acid, such as a dimerised or trimerised fatty acid. An organic trimer fatty acid having a functionality greater than 1 provides more than one reaction site with the epoxy resin serving to create a macromolecule that provides required adhesion. The aforementioned preferred carboxyl-containing polymers also provide multiple reaction sites.

The polyacid serves as a fluxing agent for the metallic powder component, removing metal oxide from the metallic powder component. This removal of the metal oxide permits the metal particles to coalesce and

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provide a continuous metal conductor. Furthermore, the removed metal oxide is produced in sufficient quantity that, in the presence of applied heat, it catalyses a reaction between the epoxy resin and the carboxyl groups on the polyacid.

Another beneficial property of the carboxylated polymer/epoxy composition is the stability of the composition with respect to reaction and curing during storage under ambient conditions. This composition is capable of extended shelf life - greater than six months at ambient temperatures.

The carboxyl groups on the polymer are non reactive at ambient temperatures. The composition will only become reactive and cross link when in the presence of heat and catalyst. Catalysts for this reaction are metal oxides, metal salts, and imidazole materials. These catalysts are generated by heating the metal powders, which oxidise to produce oxides, the oxides possibly reacting with resin and/or solvent to produce salts. Alternatively, the catalysts may be made available with the thermal release of chelating agent (an imidazole) which may have been used to protect and deactivate the copper metal. The catalysts liberated are typically: lead oxide, stannous oxide, organic tin and copper salts, and benzotriazole.

The polyacid, particularly when a polycarboxylic acid, is preferably thermally stable at 215°C and has an acid number greater than 200 and a viscosity of less than 10 centipoise at 200°C. Preferably such polymer is a carboxyl containing polymer, in particular a styrene acrylic acid copolymer. The conductive ink composition preferably contains from 5 to 25% in total of epoxy resin and polyacid and from 95 to 75% weight of the metallic powder component. More especially, one part by weight of the mixture of polyacid and epoxy resin as used is mixed with approximately 9 parts by weight of metal powder component.

Insofar as the metal powder component is concerned, the relatively low melting point constituent includes a first metal and a second metal, with the first metal having an affinity for the high melting point constituent, an oxide of the second metal being a catalyst for the curing of the epoxy resin and the first and second metals being melted together to form a metal film in which is embedded particles of the high melting point constituent while the first and second molten metals form a matrix regions between the particles of the high melting point constituent, which matrix is rich in the second metal of the relatively low melting point constituent. In such a case in particular, especially when the epoxy resin is a constituent of the ink composition, the epoxy resin is preferably liquid at ambient temperature.

The preferred metal powder component will be a mixture of three metals. One metal is the high melting point constituent of high electrical conductivity and is typically selected from copper, gold, silver, zinc, aluminium, platinum, palladium, beryllium, rhodium, nickel, cobalt, iron, molybdenum, tungsten and/or a high melting point alloy of two or more of these metals. Such metal is preferably copper powder in the particle size range from 5 to 25 μm , more preferably normally 10 μm copper.

The relatively low melting point component then provides the other two metals. One of these metals is typically tin, lead, bismuth, cadmium, zinc, gallium, indium, tellurium, mercury, thallium, antimony, selenium and/or an alloy of two or more such metals. The preferred such metal is tin although, when a third metal is not present, it can be lead. When a third metal is present, this is preferably lead and then the two metals constituting the relatively low melting point component are preferably tin/lead (Sn-Pb), preferably as eutectic alloy (Sn 63). The particle

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size of this lower melting point metal component is preferably also in the range of from 5 to 25 μm , being nominally 10 μm powder.

Additional components not hitherto specified may be present in the conductive ink compositions of this invention. Thus, improved performance is achieved when the copper powder which is preferably used as the high melting metal powder is cleaned and coated with a stability enhancer which is an organic chelation agent, preferably an azole such as benzotriazole whose decomposition products are also catalysts for the reaction between the epoxy resin adhesive and the polyacid and serve to bring about high density cross-linking without the need for any post-curing.

One further additional compound which may be present in the conductive ink composition is a reaction accelerator, preferably benzotriazole. Such azole compounds may be used to chelate metal, in particular copper, and are then released into the polymer matrix at the activation temperature, to serve as a catalyst to crosslink the epoxy/polyacid composition rapidly, providing a "snap cure" of the adhesive system present in a continual process. No post cure or further treatment is necessary.

In considering the use of the conductive ink composition embodying this invention, the following diverse chemical principals should be borne in mind:

- (i) the low melting point metal component is preferably a tin/lead alloy which is oxidizable and has a lower melting temperature than the preferred high melting point metal, copper;
- (ii) tin, as preferred low melting point metal, has, in its molten state, a particularly good affinity for copper;

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- (iii) tin and lead form, when melted together, a metal film;
- 5 (iv) the polyacid, preferably styrene acrylic acid copolymer, will flux both copper and tin/lead alloy;
- 10 (v) lead oxide and the decomposition products from benzotriazole are catalysts for the reaction between the epoxy resin adhesive and the polyacid; and
- 15 (vi) finally, and this is important in considering the stability of the conductive ink, copper powder catalyses the reaction between the epoxy resin and the polyacid. This needs to be eliminated or at least slowed down at ambient temperature.

20 In the production of printed circuit boards, the conductive ink is patterned on a dielectric substrate, which is normally pre-patterned with the epoxy resin when the epoxy resin is not present in the ink, patterning being effected, in general, by a screen

25 printing process. The substrate, with ink applied, is then heated in an oven, preferably in a vapour phase oven that transfers heat quickly, to a temperature that is (1) above the lower melting temperature of the relatively low melting metal component but (2) less

30 than the relatively higher melting temperature of the first metal, the respective metals being preferably tin/lead and copper. Unless otherwise indicated, these two metal components will be presented hereinafter as representative low and high melting point constituents

35 as aforesaid. With these representative components, in particular, heating may be at 215°C for five minutes.

The high melting metal component (i.e. copper) and

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the metal alloy powder (tin/lead) are both strongly fluxed by the polyacid which permits the molten tin to wet the surface of the copper. The chelate compound releases material from the surface of the Cu powder providing clean solderable copper surfaces. The tin/lead matrix becomes, in regions between the particles of the copper, rich in lead. A molten metal film coalesces, expelling both the epoxy resin and the polyacid to the surfaces of the film. Epoxy resin present in contact with the surfaces of the metal film is catalyzed by the metal oxide salts and possibly benzotriazole now present at the surface of the metal matrix and becomes rapidly cured and cross-linked. In the meanwhile, all of the acid groups will have reacted with the epoxide groups so as to neutralize the polyacid groups. A highly-electrically-conductive metal film strongly adhering to the dielectric substrate by a non-corrosive cured epoxy composition is then produced.

Thus, two conflicting objectives are satisfied, namely (1) a strong fluxing action which requires both a highly active reducing agent and a highly flowable low viscosity matrix, and (2) a reaction involving the polymer resin which is effective both to neutralise and immobilize the system while achieving adhesion to the substrate. Both of these are met.

The achievement of these objectives is met specifically by the conductive ink composition showing synergism when used in the manufacture of printed circuits. Thus (1) the polyacid of the conductive ink serves as a very effective chemical and mechanical flux for (2) the metallic content of the conductive film, permitting coalescing of the high melting point metal component powdered particles within a metal film as a continuous conducting body having excellent electrical and mechanical properties. During curing of the epoxy resin, an oxide is present on the surface of the

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metallic film and serves to catalyse curing and cross-linking of this resin-adhesive material and neutralizing of its acidity. Thus, one component promotes a change in the other component and vice versa. The net result of this synergism between resin-adhesive and the metallic components of the conductive ink composition is to produce a high quality metal film that may be strongly adhered to a dielectric substrate by a non-corrosive cured epoxy adhesive.

There is no wastage of materials in the production of printed circuits insofar as the conductive ink is concerned. Moreover, there is no emission of environmentally-harmful liquids or gases. The conductive ink itself is safe, non-toxic and stable on storage. The mechanical and electrical properties of the electrical circuit traces produced with the conductive ink match in quality those of normal (copper) printed circuit traces, typically exhibiting resistivity of less than 25 milliohms per square (at a thickness of 25 μ m), more preferably less than 10 milliohms per square (at a thickness of 25 μ m). Only small quantities of the conductive ink are required. In itself, the conductive ink is economical both for manufacture and use.

In accordance with the aforementioned fourth aspect of the invention, the stability and shelf life, or pot life, of conductive inks embodying this invention is greatly extended, typically by more than one order of magnitude, by taking certain steps in their preparation.

Firstly, when the high melting metal powder of the conductive ink is a copper powder, it is chelated with a very thin coating of a copper deactivator such as benzotriazole applied to the individual particles of the powder. This coating retards oxide or salt formation. The same chelation also serves desirably to prevent the catalytic effect of the high melting metal,

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especially copper, in promoting prematurely the cross-linking of the resin. Upon release from the copper at activation temperature, the benzotriazole acts as a powerful catalyst for the curing reaction.

5 Secondly, an anti-oxidant copper deactivator, preferably oxalyl bis benzylidene hydrazine, is added to the resin to retard further the cross-linking reaction to which the resin is susceptible. The preferred oxalyl bis benzylidene hydrazine exhibits an
10 inhibitory effect in a copper-containing epoxy resin reacted with a carboxylic resin by exhibiting a greater affinity for the unavoidably occurring copper salts than does the resin. Shelf life of copper-containing resin conductive ink, in particular, is typically
15 increased by the aforementioned more than one order of magnitude when the inhibitor is present in the resin in a preferred concentration in the range of 0.25% to 5%, more preferably 1%, by weight.

20 For a better understanding of the invention and to show how the same may be carried into effect, reference will now be made to the accompanying drawings to be referred to in the following description and the working examples, in particular. In the drawings:

25 Figure 1 is a diagrammatic representation of a cross-section through an epoxy resin-containing conductive ink embodying this invention when applied to a substrate but prior to heating thereof to cause flow of the relatively low
30 melting metal constituent;

 Figure 2 is a like view to that of Figure 1 but showing the condition of the ink after flow has occurred;

35 Figure 3 shows in greater detail a typical portion of the applied ink after such flow has taken

place, showing the constitution of different zones within the ink composition;

5 Figure 4 is a photomicrograph at 150x magnification of a printed /sintered ink embodying the invention over bare FR4 substrate.

10 Figure 5 is a photomicrograph at 300x magnification of a printed /sintered ink embodying the invention over a gold/nickel pad.

Conventional printed circuits are made by subtractive procedures in which circuit boards are laminated with one or more conductive layers which are
15 etched to remove some portions of the conductive layer, leaving other portions according to a pre-determined circuit design. The technique involves relatively complex photographic procedures requiring large capital investments for etching and plating equipment and
20 related apparatus, such as cameras. In general, the time required to design and produce a printed circuit by such conventional techniques is quite long and requires the use of skilled technicians. As a result, relatively few companies are capable of producing
25 printed circuits using conventional techniques. Moreover because of the time and expense involved in preparing a printed circuit, standard procedures are not generally appropriate for short production runs, notwithstanding the desirability of the aimed printed
30 circuit. The method of this invention is of assistance in enabling such reservations to be set aside, particularly because it enables screen printed technologies to be adopted.

35 When producing a conductive ink composition embodying this invention, the resin-adhesive component, when a component of the composition, is first mixed with the polyacid component. This mixture, or the

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polyacid alone, as the case may be, and the optional exothermic compound, if used, is mixed with the constituents of the metallic powder component. The relatively low melting constituent thereof is susceptible to oxidation and is preferably an alloy of tin and lead in which it is the lead which is particularly subject to oxidation. Tin in such an alloy has an affinity for the high melting metal constituent. The oxide as aforesaid is a catalyst for the curing of the epoxy resin adhesive. The relatively low melting constituent of the metallic powder component is to form a metal film on melting.

Hereinafter, again, the invention will be described primarily with respect to the use of copper as high melting metal and a tin/lead alloy, in particular Sn 63, as relatively low melting constituent and the inclusion of epoxy resin in the ink. As already noted, the preferred tin/lead alloy is preferably of a particle size of 25 μm or less and is preferably of a particle size less than 10 μm . The particles of this and other low melting constituents are preferably first cleaned using, for example, a technique to be described in the examples which follow. Such cleaning is preferably to be applied to the high melting metal constituent. The acidic epoxy adhesive component, i.e. mixture of polyacid and epoxy compound, (and any optional exothermic compound) of the conductive ink preferably constitutes from 5 ~ 25% by weight thereof and the metallic powder component preferably constitutes from 95% ~ 75% by weight thereof. The acidic epoxy adhesive component is particularly preferably present in an amount of 10% by weight of the conductive ink and the metal powder component is then preferably present in an amount of approximately 90% by weight.

Insofar as the metallic powder constituent is concerned, preferably the higher melting point metal

(normally copper) constitutes up to 90% by weight, more preferably 67% by weight of the component. The preferred metal alloy component (normally tin/lead) preferably amounts to from <100% to 10% by weight, more preferably amounting to 33%.

The stability of conductive inks embodying this invention during storage and use may be maintained for relatively long periods, and for generally longer times than heretofore. This improved stability helps minimise quality problems in the production of printed circuits using the inks. Improved stability may be achieved in one or both of two ways.

Firstly, the high melting metal component, normally copper powder, is chelated with an organic coating, preferably a benzotriazole in an extremely thin coating over the individual particles. This coating neither affects the electrical conductivity nor degrades the solder wetting characteristics of the powder. Such chelating coatings are well known in the art as a means of preventing oxide formation on copper materials and are commonly used to maintain the solderability of copper lands on printed circuit boards. Such coatings have also been employed in copper powder paints to reduce oxidation and to maintain electrical conductivity when conductivity is dependent upon physical contact between individual metal particles in the powder since oxide formation reduces conductivity.

However, in the practice of the present invention, the chelation of the copper also serves to prevent the catalytic effect of the copper in promoting the cross-linking of the resin.

Moreover, a novel anti-oxidant copper deactivator may be added to the resin to enhance such inhibition of catalytic effects of the copper on the cross-linking of the resin. A preferred such deactivator is oxalyl bis benzylidene hydrazine. Copper deactivators, such as

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this compound, have previously found commercial application in preventing embrittlement of polyethylene hook-up wire when it comes into contact with copper metal. This embrittlement was caused by an oxidated cross-linking and degrading of the polymer by copper salts. However, no previous use of a copper deactivator in combination with epoxy resin has hitherto been described.

The preferred oxalyl bis benzylidene hydrazine material exhibits an inhibitory effect in a copper-containing epoxy resin reacted with a carboxylic resin. The inhibitor is effective by its exhibiting a greater affinity for the copper salts than the resin. Shelf life of copper-containing resin conductive ink is then typically increased by more than one order of magnitude when the inhibitor is present in the resin in a preferred concentration in the range of 0.25% to 5%, more preferably 1% by weight.

A printed circuit board may be produced using the conductive ink of the invention by patterning on a dielectric substrate, normally by a screen-printing process. The applied ink will have the appearance shown in cross-section in Figure 1. The substrate with the conductive ink composition patterned thereon is then heated to a temperature intermediate the melting points of the two constituents of the metallic powder component. The acid component then serves as a fluxing agent to the oxidizable higher melting metal powder as well as for the relatively low melting metal constituent. It removes oxide from the surface of particles of the metals present, permitting the relatively lower melting point metal to wet the surface of the first metal to which it has a considerable affinity when the respective metals are tin and copper. The ink will now be as shown in Figure 2. Figure 3 shows the condition of the ink in greater detail with reference to the use of Cu and Sn63/Pb37 for the two

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metal powders.

The present invention has been described generally herein with respect to the additive provision of circuit patterns by printing of the inventive ink on a dielectric substrate with epoxy resin being present either in the ink or as a coating applied to the substrate and serving to act as an adhesive for the patterned circuit to the substrate. This principle may also be applied to the production of multilayer printed wiring boards in which a plurality of layers is produced in accordance with the method of the invention and laminated together with interposition of dielectric layers between conductive layers. The metal traces produced must here be resistant to melting when further heating takes place to achieve bonding together of the layers. Particularly with such multi-layer structures, there is a need to provide interconnections between the circuits of individual layers. Vias for this purpose are typically formed in a PCB by for example drilling, punching, laser drilling or etching in a circuit after an adhesive has been applied to the dielectric side of the circuit, and provide electrical connection between circuits at different levels in an overall structure or serve merely to provide a connection between applied components and a printed circuit. There is a need for there to be a good filling degree of conductive material in the via and good adhesion of such material to the wall of the via. Via filling compositions are frequently of a pasty nature and enter the vias by application of a via-filling composition to the printed circuit board and application of a doctor blade to ensure entry into the via. Compositions embodying this invention which contain an epoxy resin meet the aforesaid requirements of via formation eminently owing to the quality of adhesion attainable through the presence of metal oxide produced on reaction between the polyacid fluxing agent and the metal powder, which

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adhesion may be enhanced as a result of other cross-linking enhancing factors described hereinabove.

Thus, this invention also provides a multilayer wiring board in which vias connecting electrically
5 conductive circuits contain a metal filling resulting from filling the vias with a composition according to the first aspect of the invention having the epoxy resin contained therein and heating to a temperature between said first and second temperatures to cure and
10 crosslink the epoxy resin and cause the via filling to adhere to the via walls.

Although reference has been made hitherto to the printing of compositions embodying this invention on a dielectric substrate and the achieving of a good
15 adhesion thereto, adhesion may be enhanced by provision of channel formations patterned on the substrate.

Thus in one procedure, the epoxy resin is pre-coated on the dielectric substrate, a photoimageable layer is applied to the adhesive layer, the
20 photoimageable layer is subjected to a photoimaging and developing process to form a channel pattern in the photoimageable layer corresponding to the circuit, said admixture is introduced into the channel pattern and the dielectric substrate is heated to said temperature
25 to achieve substantially complete crosslinking of the epoxy resin.

In an alternative procedure, a photoimageable layer is applied to the dielectric substrate and subsequently subjected to a photoimaging and developing
30 process to form a channel pattern. Said admixture, additionally containing the epoxy resin, is introduced into the channel pattern and the dielectric substrate is heated to said temperature to achieve substantially complete crosslinking of the epoxy resin.

35 This principle of channel patterning may be applied to each of the plurality of layers involved when producing a multilayer wiring board. Further

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particulars of the channel patterning technique are to be found in WO-96/22670.

5 The compositions of this invention find use in a number of areas of electronics and PCB/wiring board technology to be described hereinafter. Specific circuit features to be indicated hereinafter will be formed of a composition embodying this invention having the epoxy resin incorporated therein and will have been heated in-situ to a temperature sufficient to melt the
10 relatively low melting point constituent but below the melting point of the high melting point constituent, being a temperature at which the polyacid is thermally stable, to achieve metallic sintering and substantial crosslinking of the epoxy resin.

15 For example, the compositions of this invention may be used in this way as an alternative to soldered wires for the repair and/or modification of conventional etched copper printed wiring boards.

20 Although described primarily as having use in the production of laminar circuits as in printed circuit boards, because compositions embodying this invention have practical use as polymer thick films, the composition may then have a structural function. For example the compositions may be employed in the
25 formation of thermal transfer pillars in the construction of semi-conductor packages, multichip modules, etc. The compositions may also be used to form conductive terminations for printed potentiometer tracks giving extremely low contact resistance through
30 the wiper of the potentiometer assembly by being extremely resistant to wear.

Particularly insofar as the compositions of the invention may provide a conductive adhesive, they may then function as a replacement for solder in the
35 joining of electronic components to conductive "lands" on substrates. The compositions may also be utilised to operate simultaneously as conductive tracers and as

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conductive adhesive on a substrate, thus requiring no "lands" for the electrical connection of electronic components. In this case, cross-linking should not be completed before applying the electronic components.

5 A further area of use of compositions involving this invention is as a shielding layer on printed wiring boards for the suppression of electromagnetic interference (EMI)/radio-frequency interference (rfi). Such uses have particularly relevance to the production
10 of cellular telephones.

The invention may be better understood by reference to the following examples which are intended for purposes of illustration and are not to be construed as in any way limiting the scope of the
15 present invention, which is defined in the claims appended hereto. The following materials were used when carrying out the Examples:

	<u>Materials</u>	<u>Source</u>
20	SnPb solder alloy (63:37), 10-25 μ m particle size	Multicore Solders Ltd.
	Copper powder, <20 μ m particle size	ACuPowder International
	Entek Plus 106A,	Enthone-OMI
25	benzotriazole passivation system for copper	
	"SF-50" silver flake, \leq 0.4 μ m particle size, optionally added to the ink	
30	formulation to modify rheology Joncryl 682, styrene-acrylic copolymer which is the cross-linking agent and primary fluxing agent	Degussa SC Johnson
35	Epikote 862, (uncrosslinked) epoxy resin	Shell
	OABH inhibitor, anti-oxidant	

copper deactivating agent
(oxalyl bis benzylidene
hydrazine) Eastman
Modaflo, a rheology modifier
5 optionally added
to formulations to enhance
flow of epoxy resin prior to
cross-linking Monsanto
Silquest A-187 Silane,
10 a coupling agent optionally
added to formulations to
promote better adhesion OSI Specialties
3, 3-Thiodipropionic acid,
an optional secondary
15 activator
Butyl carbitol, solvent Aldrich

Inks were prepared in several stages in the Examples:

- * metal powder preparation
- 20 * styrene-acrylic copolymer solution preparation
- * activator system preparation
- * ink base preparation
- * fully formulated ink preparation
- * final adjustment of ink.

25

Example 1

Preparation of Metal Powders

The copper powder was immersed in 5% v/v sulphuric
acid at 80°C until it exhibited a bright salmon
30 colouration. It was then collected by filtration and
thoroughly rinsed with deionised water and dried. Cleaned
copper powder was treated with Entek Plus 106A. The
solder powder was cleaned in a 10% w/w aqueous solution of
ammonium bifluoride before being collected, rinsed and
35 dried.

Preparation of Styrene-Acrylic Copolymer Solution

50 g of butyl carbitol were added to 100 g of Joncryl

682. This mixture was stirred over a hotplate at 120°C until a clear pale yellow solution was obtained. This was stored in an air tight bottle at room temperature pending use in the next stage.

5 Preparation of Ink Base

75 g of the styrene-acrylic copolymer solution were placed in a 400 cm³ beaker. 50 g of Epikote 862 were added, along with 0.5 g of Modaflo, 0.25 g of Silquest A-187 and 1.0 g OABH. This mixture was homogenised with a spatula and stored in a sealed plastic jar pending ink preparation.

10 Preparation of Activator System

The styrene-acrylic copolymer solution did not confer sufficient fluxing activity. Therefore, a secondary activator was incorporated. This was prepared as follows:

5 g of 3,3-thiodipropionic acid were added to 10 g of butyl carbitol. The mixture was warmed to form a colourless solution (although there was precipitation on cooling).

20 Preparation of Fully Formulated Ink

10 g of ink base was weighed into a 125 cm³ beaker. 60 g of cleaned/passivated copper powder, and 30 g of cleaned solder powder were added. These ingredients were mixed with a spatula for about ten minutes.

25 Final Adjustment

The rheology of the ink was adjusted to facilitate printing by the addition of extra butyl carbitol and SF-50 silver flake.

Sintering was investigated by floating a thin film of ink smeared across a microscope slide on a solder bath at 235°C. Sintering (ie solder-copper wetting) is indicated by a change in colour from brown to grey. This only occurred when a small amount of the prepared activation system was added; this was first homogenised in view of the precipitation which occurred.

35 Assessment of Fully Formulated Ink

The composition of the fully formulated ink is given

in Table 1.

Table 1: Composition Of The Fully Formulated Ink

All data are in wt%.

Ink Component	Amount
Ink base	9.70
Activator system	0.77
Butyl carbitol	1.90
Copper powder	58.10
Solder powder	29.00
SF50 silver flake	0.48
Activator System	
3, 3-Thiodipropionic acid	33.33
Butyl carbitol	66.67
Ink Base	
Styrene-acrylic copolymer solution	59.15
Epikote 862	39.45
Modaflo	0.40
Silquest A-187	0.2
OABH	0.80
Styrene-acrylic copolymer solution	
Joncryn 682	66.67
Butyl carbitol	33.33

The ink was assessed in several ways:

- * fineness of grind
- * viscosity profile
- * printing characteristics
- * electrical properties of sintered ink

The fineness of grind measurement indicated some agglomerated particles above 50 μ m. These broke down during testing.

Ink viscosity at 25°C was measured using a Brookfield HBT viscometer fitted with a an SC4-14/16R spindle. The results are tabulated in Table 2:

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Table 2

Speed (rpm)	Fineline Ink (cps)
1	250,000
2.5	200,000
5	180,000
10	150,000
20	130,000
50	90,500
100	69,000
50	80,000
20	100,000
10	120,000
5	140,000
2.5	160,000
1	200,000

To test printing characteristics, ink was printed with a DEK245 printer onto FR4 substrate which had been degreased with acetone and stored for two days in an air-circulating oven at 60°C to remove trapped moisture. Three screens were used. The results are shown in Table 3.

Table 3

<u>Screen</u>	1	2	3
Mesh/inch	180	180	230
Mesh type	Stainless steel	Stainless steel	Stainless steel
Mesh orientation/°	90	45	90
Emulsion thickness	15 (97-112)	12 (95-107)	12 (77-89)/μm

Printing parameters

Printer speed	44	44	44
/mm s ⁻¹			
Squeegee type	Diamond, 45°	Diamond, 45°	Diamond, 45°
Squeegee pressure	5.5-5.6	4.6-4.7	6.1-6.2
/Kg			

Substrate type

Blank FR4	Cu / FR4	Blank FR4
	Au/Ni/FR4	

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The ink rolled well on all screens with no skidding. Print definition was good, and there was no bleeding with two of the three screens. Four thou lines with the third screen were ill defined, probably due to the FOG (four thou = 100 μ m, i.e. twice the size of some agglomerated particles); in addition, there was very slight bleeding.

Printed PCBs were dried for 5 minutes in an air-circulating oven at 120°C to remove solvent. The thickness of the dried ink was then measured using a Taylor-Hobson Talysurf 10 surface texture measuring instrument:

Screen	1	2	3
Thickness/ μ m	40-42	56-58	32-35

Finally, printed PCBs were reflowed in a vapour phase reflow oven at 215°C for 4 minutes with a short (1 minute) dwell time at 50°C before and after.

Successful flow of the solder to achieve a coalesced metal film was achieved in all cases. Further measurements using the Taylor-Hobson Talysurf 10 surface texture measuring instrument indicated no modification in print thickness.

The sintered ink was assessed for electrical resistivity using a four-probe method, with the print thickness normalised to 25 μ m:

Screen	3	1
Resistivity	10.5	15
/mOhm/square		

Solderability was investigated by applying low solids liquid flux to the sintered ink, followed by brief exposure to 60/40 Sn/Pb solder at 235°C. The sintered ink was successfully soldered.

The character of the conductive layer was

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investigated by microscopic examination of a sectioned specimen at 300x magnification (Figure 4). This suggested a good degree of metal fusion. Ability to wet metallic surfaces during sintering was assessed using the patterns printed with Screen 2 (Figure 5). Both the copper and gold surfaces became coated with solder. This is important in considering the present invention as a conductive "adhesive" for joining electronic components to printed circuit boards.

Finally, there was a brief shelf life study. A one gram sample was placed in a air circulating oven at 60°C for 24 hours. There was no sign of modified physical properties or premature curing.

Example 2

A specimen of the ink from Example 1 was successfully sintered under air using a Sikama hot belt reflow station. The resistivity was the same as that given by an identical sample sintered in parallel using a vapour phase reflow oven.

Examples 3-6

Following the success of the preceding examples, further batches of ink were prepared in the same manner as in Example 1 and used to investigate the role of the various components and metal powder treatments. Typical data given in Table 4 underline the complexity of the formulation process with both composition and treatment impacting upon stability, sintering capability and resistivity. The data presented are for illustrative purposes only.

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Table 4: Modification of Ink Composition

All amounts are in grams.

Example	3	4	5	6
Ink base				
Styrene-acrylic copolymer solution*	29.58	29.58	29.58	29.58
Epikote 862	19.72	19.72	19.72	19.72
Modaflo	0.2	0.2	0.2	0.2
Silquest A-187	0.1	0.1	-	-
OABH	-	0.4	-	0.4
3,3-Thiodipropionic acid	0.13	0.13	0.13	0.13
Butyl carbitol	1.2	1.2	1.2	1.2
Ink base properties				
Viscosity at 20rpm/cP	8500	8900	11200	9400
Stability after 2 weeks	OK	OK	OK	OK
Stability after 8 weeks	Becoming thick	Slightly sticky	Slightly sticky	Slightly sticky
Ink				
Ink base	5.00	5.00	5.00	5.00
Copper powder	22.50	22.50	30.00 ¹	30.00 ²
Solder powder	21.35	21.35 ²	14.23 ²	14.23
Extra butyl carbitol	1.50	-	1.50	-
Ink properties				
Stability after 1 week	Slight skin		Poor	PoorOK
Stability after 3 weeks	Early cure stage		-	--
Sintering capability	90%	None	70%	50%
Resistivity of sintered ink / mOhm/square/25 μ m	18.8	3132	19.8	25.5

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- * Exactly the same as in the first example.
- 1 Copper cleaned and Entek Plus 106A coated
(otherwise copper is cleaned but not passivated)
- 2 Cleaned solder alloy

5

A prerequisite for all chemicals used in the manufacture of electrical products is ionic cleanliness: this minimises the possibility of in-service reliability problems. Therefore, inks sintered during this stage of the product development process were also subjected to ionic contamination assessment using the Multicore CM11 Contaminometer. All exhibited low ionic contamination below $0.2 \mu\text{g NaCl eq/cm}^2$, easily in line with the demands of industry standards such as MIL-P-28809A.

10
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CLAIMS:-

1. A composition of matter comprising
 - (a) a metal powder,
 - (b) a solder powder,
 - 5 (c) a polymer or a monomer which is polymerisable to yield a polymer, a said polymer being crosslinkable under the action of a chemical cross-linking agent,
 - (d) a chemical cross-linking agent for said
 - 10 polymer, the cross-linking agent having fluxing properties and being unreactive with the polymer without catalysis, which metal powder and/or solder powder generates and/or has adhered thereto a catalyst
 - 15 (e) for the cross-linking agent which is liberated on application of heat.
2. A composition according to Claim 1, wherein said metal powder is selected from Au, Ag, Cu, Zn, Al, Pd,
- 20 Pt, Rh, Fe, Ni, Co, Mo, W, Be, and alloys thereof.
3. A composition according to Claim 2 wherein said metal powder is copper.
- 25 4. A composition according to Claim 1, 2 or 3, wherein said solder powder is selected from Sn, Bi, Pb, Cd, Zn, Ga, In, Te, Hg, Sb, Se, Tl and alloys thereof.
5. A composition according to Claim 4 wherein said
- 30 solder powder alloy is Sn63Pb37.
6. A composition according to any preceding claim wherein said latent chemical cross-linking agent is selected from carboxylated polymers, dimer fatty acids,
- 35 and trimer fatty acids.
7. A composition according to Claim 6 wherein said

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patent chemical cross-linking agent is a styrene-acrylic acid copolymer.

5 8. A composition according to any preceding claim wherein said catalyst is generated by oxidation of solder powder and liberated from the solder powder by the fluxing agent.

10 9. A composition according to Claim 8 wherein said catalyst is generated by oxidation of tin and/or lead powder and liberated from the powder by the fluxing agent.

15 10. A composition according to Claim 1 wherein said catalyst is generated by reaction of metal powder or solder powder with resins or solvent to produce organo-metal salts.

20 11. A composition according to Claim 10 wherein said catalyst is generated by reaction of tin with resin or solvent to produce tin salt.

25 12. A composition according to Claim 10 wherein said catalyst is generated by reaction of copper with resin or solvent to produce copper salts.

30 13. A composition according to any preceding claim, wherein said catalyst is an organic chelating agent adhered to the metal powder and liberated at solder melting temperature into the fluxing agent.

14. A composition according to Claim 13 wherein said catalyst is an azole chelating agent.

35 15. A composition according to claim 13 wherein said catalyst is benzotriazole

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16. A composition according to any preceding claim further comprising an organic surface protectorant chelate coating the metal for stability enhancement.
- 5 17. A composition according to Claim 16 wherein said organic surface protectorant is benzotriazole.
18. A composition according to any preceding claim further comprising a copper salt deactivator as a
10 stability enhancer.
19. A composition according to Claim 18 wherein said copper salt deactivator is oxalyl bis benzylidene hydrazine.
- 15 20. A composition on, or for application to, a dielectric substrate in a predetermined pattern comprising, in admixture:
- 20 (i) a metallic powder component which includes (a) a high melting point constituent of high electrical conductivity and (b) a relatively low melting point constituent; and (ii) a polyacid effective as a fluxing agent for the metallic powder component and as a cross-linking agent for
25 an epoxy resin at a first temperature and at a higher second temperature, respectively, the polyacid being in contact with such epoxy resin.
21. A composition according to claim 20 which has the
30 epoxy resin in admixture with the metallic powder constituent and the polyacid.
22. A composition according to claim 20, which has the epoxy resin pre-applied to the dielectric substrate.
- 35 23. A composition according to claim 22, wherein the epoxy resin is printed on the substrate in a

predetermined pattern.

24. A composition according to any one of claims 20 to 23, wherein the polyacid is thermally stable to 215°C and has an acid number greater than 200 and a viscosity less than 10 centipoise at 200°C.

25. A composition according to one of claims 20 to 24, wherein the polyacid is a polycarboxyl compound which serves as a fluxing agent for the metallic powder so as to produce a metal oxide which, in turn, is a catalyst for the reaction between the epoxy resin and carboxyl groups of the carboxyl-containing polymer at said second temperature.

26. A composition according to claim 25, wherein the polycarboxyl compound is selected from: carboxylated polymers, polycarboxylic acids and polymer fatty acids.

27. A composition according to claim 26, wherein the polymer fatty acid is a dimer or trimer fatty acid.

28. A composition according to claim 26, wherein the carboxylated polymer is a styrene-acrylic acid copolymer.

29. A composition according to any one of claims 20 to 28, wherein the metal powder component contains up to 0 to 80% by weight of the high melting point constituent of high electrical conductivity and from <100 to 20% by weight of the relatively low melting point component.

30. A composition according to any one of claims 20 to 29, wherein the high melting point constituent of the metallic powder component is a metal selected from Au, Ag, Cu, Zn, Al, Pd, Pt, Rh, Fe, Ni, Co, Mo, W, Be, and alloys thereof.

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31. A composition according to any one of claims 20 to 30, wherein the low melting point constituent of the metallic powder component is selected from Sn, Bi, Pb, Cd, Zn, Ga, In, Te, Hg, Sb, Se, Tl and alloys thereof.

5

32. A composition according to any one of claims 20 to 31, wherein the relatively low melting point constituent includes a first metal and a second metal, with the first metal having an affinity for the high melting point constituent, an oxide of the second metal being a catalyst for the curing of the epoxy resin and the first and second metals being melted together to form a metal film in which is embedded particles of the high melting point constituent while the first and second molten metals form a matrix in regions between the particles of the high melting point constituent, which matrix is rich in the second metal of the relatively low melting point constituent.

10

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20

33. A composition according to claim 32, wherein the relatively low melting point constituent is a tin/lead alloy.

25

34. A composition according to claim 33, wherein the high melting point constituent is copper.

35. A composition according to any one of claims 20 to 34, wherein the metallic powder component has particles of a size less than 25 μ m.

30

36. A composition according to any one of claims 20 to 33, wherein the epoxy resin consists essentially of an epoxy resin which is liquid at ambient temperature.

35

37. A composition according to any one of claims 20 to 36; which contains, in percent by weight, from 5 to 50% in total of epoxy resin and carboxyl-containing polymer

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and 95 to 50% of the metallic powder component.

38. A composition according to any one of claims 20 to 37 wherein the high melting point constituent is a copper powder which has been cleaned and coated with a stability enhancing copper deactivator which is a chelation agent for the copper and a high temperature catalyst for the crosslinking of the epoxy resin.

39. A composition according to claim 38, wherein the chelation agent is an azole compound.

40. A composition according to claim 39, wherein the chelation agent is benzotriazole.

41. A composition according to any one of claims 20 to 40, wherein the high melting point constituent of the metallic powder component is copper powder and the composition additionally includes anti-oxidant copper deactivating agent.

42. A composition according to claim 41, wherein the anti-oxidant copper deactivating agent is oxalyl bis benzylidene hydrazine.

43. A method of making an electrically conductive circuit on a dielectric surface comprising patterning a dielectric substrate with the admixture of metallic powder component and polyacid as specified in claim 20 with either the epoxy resin of claim 20 being pre-coated on the substrate, or the epoxy resin being incorporated in the patterned composition, and heating the dielectric substrate thus patterned to a temperature above the melting point of the low melting point constituent but below the melting point of the high melting point constituent, being a temperature at which the polyacid is thermally stable but highly

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active as a fluxing agent to achieve metallic sintering and catalyzed crosslinking of the epoxy resin.

5 44. The method of claim 43, wherein the epoxy resin is pre-coated on the dielectric surface by patterning and the composition is applied to the epoxy resin pattern by matching patterning.

10 45. A method as claimed in claim 44, wherein the epoxy resin is pre-coated on the dielectric substrate, a photoimageable layer is applied to the adhesive layer, the photoimageable layer is subjected to a photoimaging and developing process to form a channel pattern in the photoimageable layer corresponding to the circuit, said
15 admixture is introduced into the channel pattern and the dielectric substrate is heated to said temperature to achieve metallic sintering and substantial crosslinking of the epoxy resin.

20 46. A method as claimed in claim 43, wherein a photoimageable layer is applied to the dielectric substrate and subsequently subjected to a photoimaging and developing process to form a channel pattern, said admixture additionally containing the epoxy resin is
25 introduced into the channel pattern and the dielectric substrate is heated to said temperature to achieve metallic sintering and substantial crosslinking of the epoxy resin.

30 47. A method as claimed in 46 wherein the epoxy resin is coated into the channel of the dielectric substrate and "B" staged prior to the application of the admixture.

35 48. A method as claimed in claim 45, 46 or 47, wherein the track is formed with an undercut region in side walls thereof.

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49. A method as claimed in 43 wherein the epoxy resin is applied to the entire dielectric substrate and "B" staged to produce a dry handleable substrate allowing for subsequent patterning of said admixture to said substrate.

50. An electrically conductive circuit which comprises a metal film patterned upon a dielectric substrate and adhesively adhered thereto by a cured and cross-linked epoxy resin, the metal film resulting from the provision, patterned on the substrate, of a composition according to any one of claims 1 to 42 followed by heating of the composition to a temperature sufficient to melt the solder powder or low melting constituent and coalesce the metallic film produced.

51. A method of making a multilayered electrically conductive circuit by first applying and curing an insulating dielectric layer on a single layer electrically conductive circuit produced according to the method claimed in any one of claims 43 to 49 the insulating dielectric layer having vias, and forming a second electrically conductive circuit on the cured dielectric layer by the method claimed in any one of claims 43 to 49 and repeating these steps to form a required plurality of alternating dielectric layers and electrically conductive circuit layers.

52. A method according to claim 51, wherein said vias are filled with a metal filling resulting from filling them with a composition according to any one of claims 20 to 42 having the epoxy resin contained therein and heating to a temperature sufficient to melt the relatively low melting constituent, coalesce the metals present, cure the epoxy resin and cause the via filling to adhere to the via walls.

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53. A multilayer printed wiring board in which vias connecting electrically conductive circuits contain a metal filling resulting from filling the vias with a composition according to any one of claims 20 to 42 having the epoxy resin contained therein and heating to a temperature sufficient to melt the relatively low melting constituent solder powder, coalesce the metallic film, cure the epoxy resin and cause the via filling to adhere to the via walls.

54. A thermal transfer pillar in a semi-conductor package and/or a multichip module, which is formed of a composition as claimed in any one of claims 20 to 42 having the epoxy resin incorporated therein and which has been heated in-situ to a temperature sufficient to melt the relatively low melting point constituent but below the melting point of the high melting point constituent, being a temperature at which the polyacid is thermally stable, to achieve metallic sintering and substantial crosslinking of the epoxy resin.

55. An electrically conductive termination for a printed potentiometer track, which is formed of a composition as claimed in any one of claims 20 to 42 having epoxy resin incorporated therein and which has been heated in-situ to a temperature above the melting point of the relatively low melting point constituent but below the melting point of the high melting point constituent, being a temperature at which the polyacid is thermally stable, to achieve metallic sintering and substantial crosslinking of the epoxy resin.

56. A conductive track joining leads on a printed circuit board, or other substrate usually for the purpose of repair or modification, the conductive track being formed of a composition as claimed in any one of claims 20 to 42 having the epoxy resin incorporated

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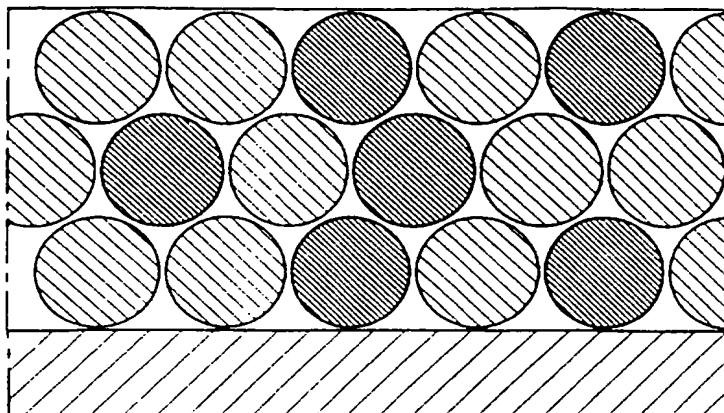
therein and which has been heated in situ to a temperature above the melting point of the relatively low melting point constituent but below the melting point of the high melting point constituent, being a temperature at which the polyacid is thermally stable, to achieve metallic sintering and substantial complete crosslinking of the epoxy resin.

57. A shield layer on a multilayer printed wiring board for suppressing of electromagnetic interference or radio-frequency interference, which layer is formed of a composition as claimed in any one of claims 20 to 42 having epoxy resin incorporated therein and which has been heated in-situ to a temperature above the melting point of the relatively low melting point constituent but below the melting point of the high melting point constituent, being a temperature at which the polyacid is thermally stable, to achieve metallic sintering and substantial crosslinking of the epoxy resin.

58. A method of joining electronic components to substrates whereby the composition as claimed in any one of claims 1 to 42 is used as an electrically conductive adhesive to adhere the electric components to a said substrate.

59. A method as described in Claim 58, where the substrate has been produced by a method as claimed in any of claims 43 to 49, 51 and 52 and the electronic components are placed into the said composition prior to the temperature being raised, the substrate is then heated to said temperature thus forming the electrically conducting circuit and joining the electronic components simultaneously to an electrically conductive circuit.

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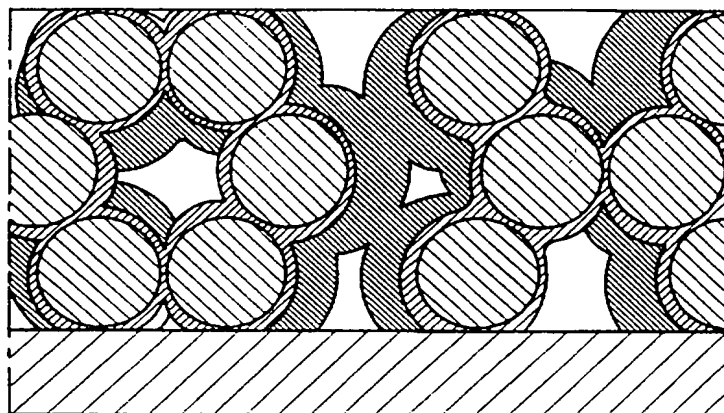
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-  Cu
-  Sn 63 / Pb37
-  FR-4 SUBSTRATE

Fig. 1








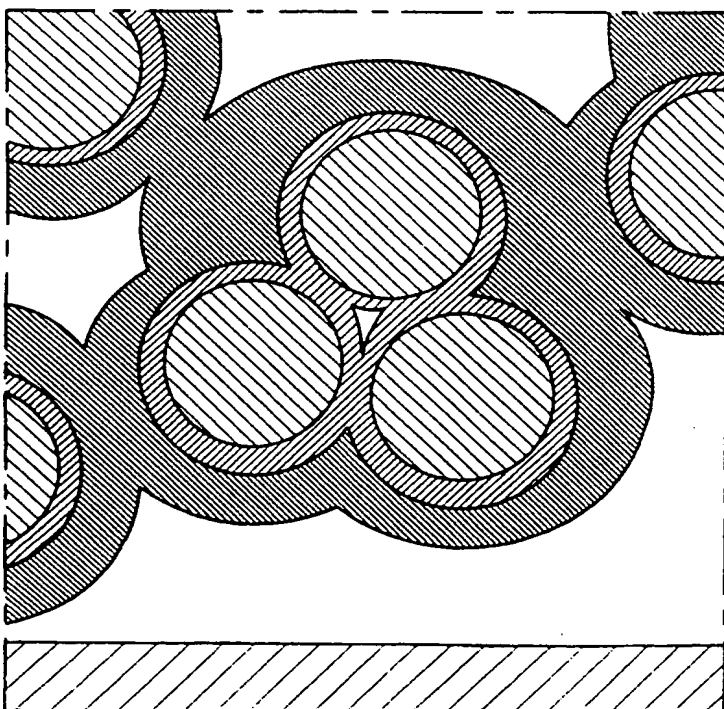
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-  FR-4 SUBSTRATE

Fig. 2








-  EPOXY RESIN
-  Cu
-  Sn 63 / Pb37
-  Cu₃ Sn / Cu₆ Sn₅
-  FR-4 SUBSTRATE

Fig. 3

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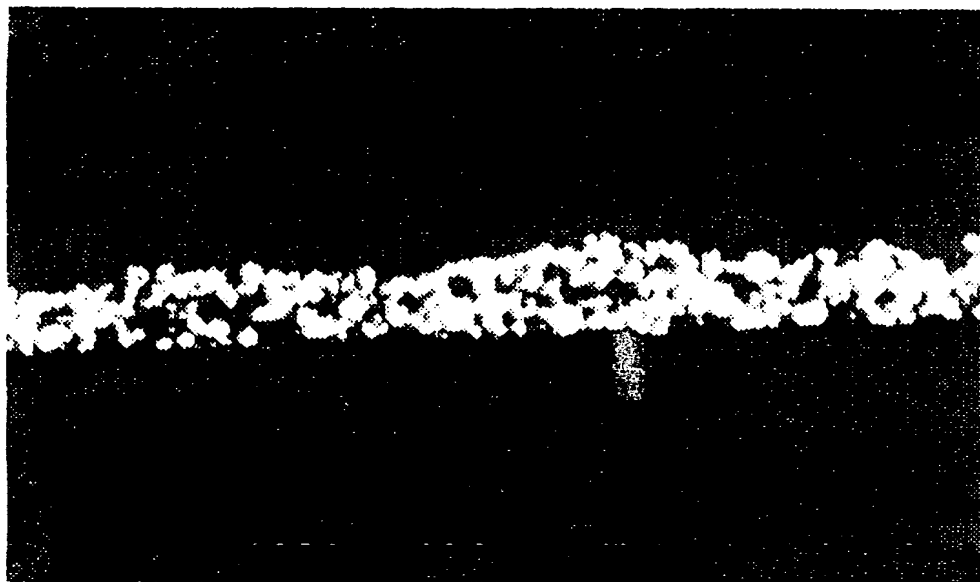


Fig.4



Fig.5

SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 97/01033

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H05K1/09 H05K3/12 H01B1/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H05K H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 376 403 A (CAPOTE ET AL.) 27 December 1994 cited in the application see column 4, line 1 - column 13, line 15 ---	1-6.20, 21, 29-37, 43, 50-53, 58
A	WO 95 13901 A (CTS CORPORATION) 26 May 1995 see page 11, line 17 - page 13, line 12 ---	1-5.20, 21, 29-34, 53
A	WO 96 13041 A (SOLAIC) 2 May 1996 see the whole document ---	1-5.20, 29-36, 43.50

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Further documents are listed in the continuation of box C



Patent family members are listed in annex

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Date of the actual completion of the international search

11 November 1997

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Mes, L

INTERNATIONAL SEARCH REPORT

Int. .onal Application No

PCT/IB 97/01033

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 5, no. 35 (C-046), 5 March 1981 & JP 55 160072 A (MATSUSHITA ELECTRIC IND CO), 12 December 1980, cited in the application see abstract ---	1-5, 20, 21, 29-34
A	DATABASE WPI Week 7901 Derwent Publications Ltd., London, GB: AN 79-01104B XP002046421 & JP 53 133 799 A (IDEA RES KK) , 21 November 1978 cited in the application see abstract ---	1-5, 20, 21, 29-34
A	WO 96 22670 A (COATES BROTHERS PLC) 25 July 1996 see page 5 - page 15 ---	20, 22, 29-35, 43-46, 48, 49
A	US 3 915 729 A (EUSTICE) 28 October 1975 see abstract ---	6, 25-27
A	US 4 663 079 A (YAMAGUCHI ET AL.) 5 May 1987 see abstract ---	13-17, 38-40
P, A	WO 96 30966 A (LITTON PRECISION PRODUCTS INTERNATIONAL) 3 October 1996 see the whole document -----	20-23, 29-35, 43, 44

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 97/01033

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5376403 A	27-12-94	AU 663342 B AU 2767892 A CA 2120523 A EP 0646048 A JP 7502369 T KR 9710170 B MX 9205644 A WO 9306943 A US 5538789 A US 5565267 A	05-10-95 03-05-93 15-04-93 05-04-95 09-03-95 21-06-97 31-08-94 15-04-93 23-07-96 15-10-96
WO 9513901 A	26-05-95	AU 1182295 A	06-06-95
WO 9613041 A	02-05-96	FR 2726001 A AU 3807495 A EP 0787347 A US 5639556 A	26-04-96 15-05-96 06-08-97 17-06-97
WO 9622670 A	25-07-96	AU 4397696 A EP 0804865 A	07-08-96 05-11-97
US 3915729 A	28-10-75	NONE	
US 4663079 A	05-05-87	JP 1743151 C JP 4034577 B JP 61040383 A JP 1797505 C JP 5006592 B JP 61078869 A DE 3564636 A EP 0170063 A US 4705647 A	15-03-93 08-06-92 26-02-86 28-10-93 26-01-93 22-04-86 29-09-88 05-02-86 10-11-87
WO 9630966 A	03-10-96	DE 19511553 A AU 5497596 A	24-10-96 16-10-96

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